Hydration Properties of Dilute Aqueous Solutions of Hydrocarbons up to the Critical Region of Water: Experimental Data and Modeling

V. Majer [C, S]
Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003 CNRS, Université Blaise Pascal, Aubière, France

J. Sedlbauer
Department of Chemistry, Technical University of Liberec, Liberec, Czech Republic

S. Degrange
Gaz de France, Saint Denis la Plaine, France

V. Hynek
Department of Physical Chemistry, Prague Institute of Chemical Technology, Prague, Czech Republic

Thermodynamic data on infinitely dilute aqueous hydrocarbons at elevated temperatures describes the evolution of interactions between a highly hydrophobic solute and water at conditions where mechanic and dielectric properties of the solvent are strongly changing. These variations are particularly pronounced in the critical region of water and are reflected by remarkable changes in the thermodynamic derivative data (enthalpy, heat capacity and volume) which exhibit the critical divergence. Understanding this extreme behaviour is both of theoretical and practical interest, namely for the development of reliable prediction schemes for petroleum chemistry and geochemistry and for design of supercritical oxidation technology. In investigating these systems it is useful to adopt the concept of hydration properties where aqueous solutes at infinite dilution are referenced to an ideal gas state. The choice of existing models for the hydration properties and new development is, however, hampered by lack of appropriate experimental data on hydrophobic solutes whose acquisition presents experimental challenges.

The purpose of this contribution is to present a new set of high-temperature data on aqueous solutions of benzene, toluene, hexane and cyclohexane and to test the models for hydration properties with the focus to the critical region of water. Heats of solution and densities for dilute systems were obtained simultaneously between 473 and 670 K and up to 33 MPa using an original apparatus "calodensimeter" combining a heat compensation mixing calorimeter with a vibrating tube densimeter in one thermostated environment [1]. The partial molar volumes at infinite dilution and the enthalpies of hydration were derived from these data by extrapolation and combined with additional thermodynamic data on hydration properties from literature. Possibilities to correlate simultaneously several hydration properties of the aqueous hydrocarbons with different models [2,3] were tested up to the critical region of water. The main purpose is to obtain reliable data on the Gibbs free energy of hydration which is of direct interest for the calculation of phase and chemical equilibria in hydrothermal systems.

[1] S. Degrange, PhD Thesis, Blaise Pascal University, Clermont-Ferrand, France (1998).
[2] J. Sedlbauer, V. Majer, Eur. J. Mineral. 12, 1109-1122 (2000).
[3] J. Sedlbauer, G. Bergin, V. Majer, AIChE J. 48, 2936-2959 (2002).